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Integration of Nafion^{Z_M} sample conditioner into existing FEM ozone monitor

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Ozone Session – Wednesday August 24, 2022

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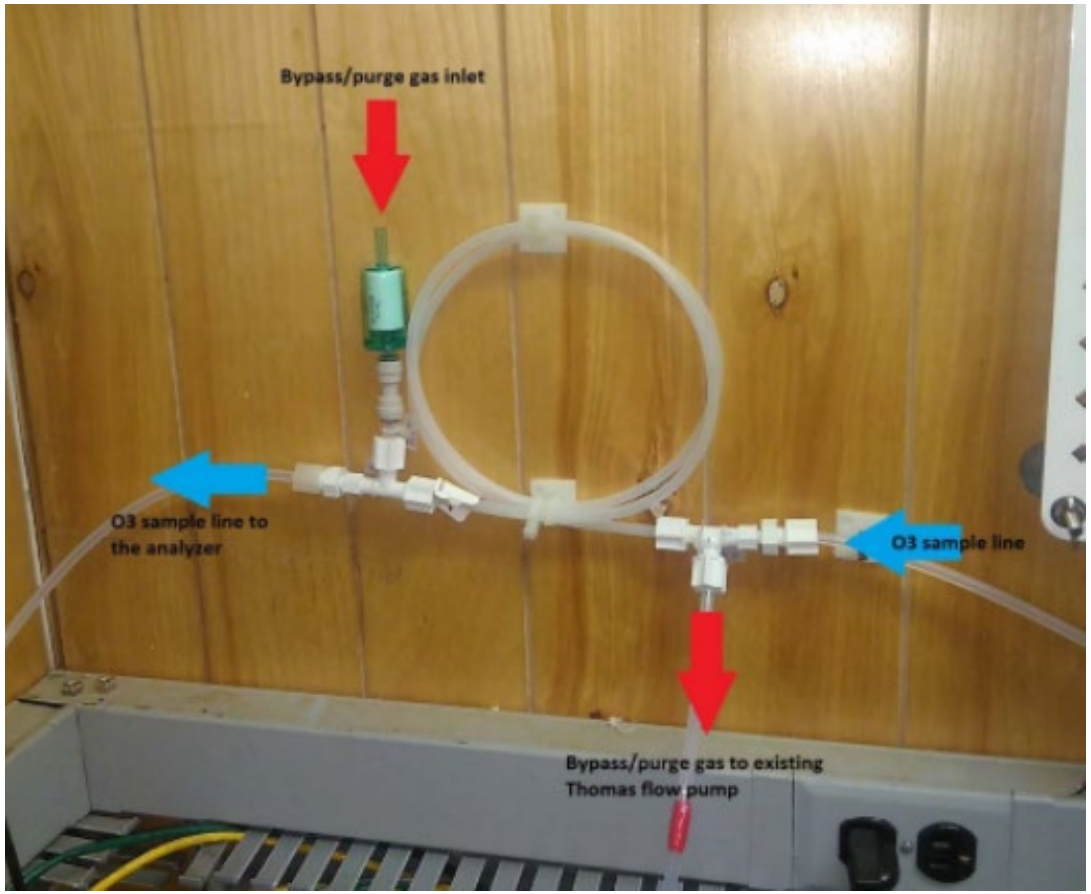
History

- EPA CASTNET program requested approval for addition of Nafion^{Ż} dryers to ozone analyzers to mitigate interference from ambient water vapor.
- EPA's CASTNET contractor performed testing in Gainesville, FL from October 2016 through 2017.
- Testing with dryer showed improved response
  - less noise
  - faster response
  - less interference

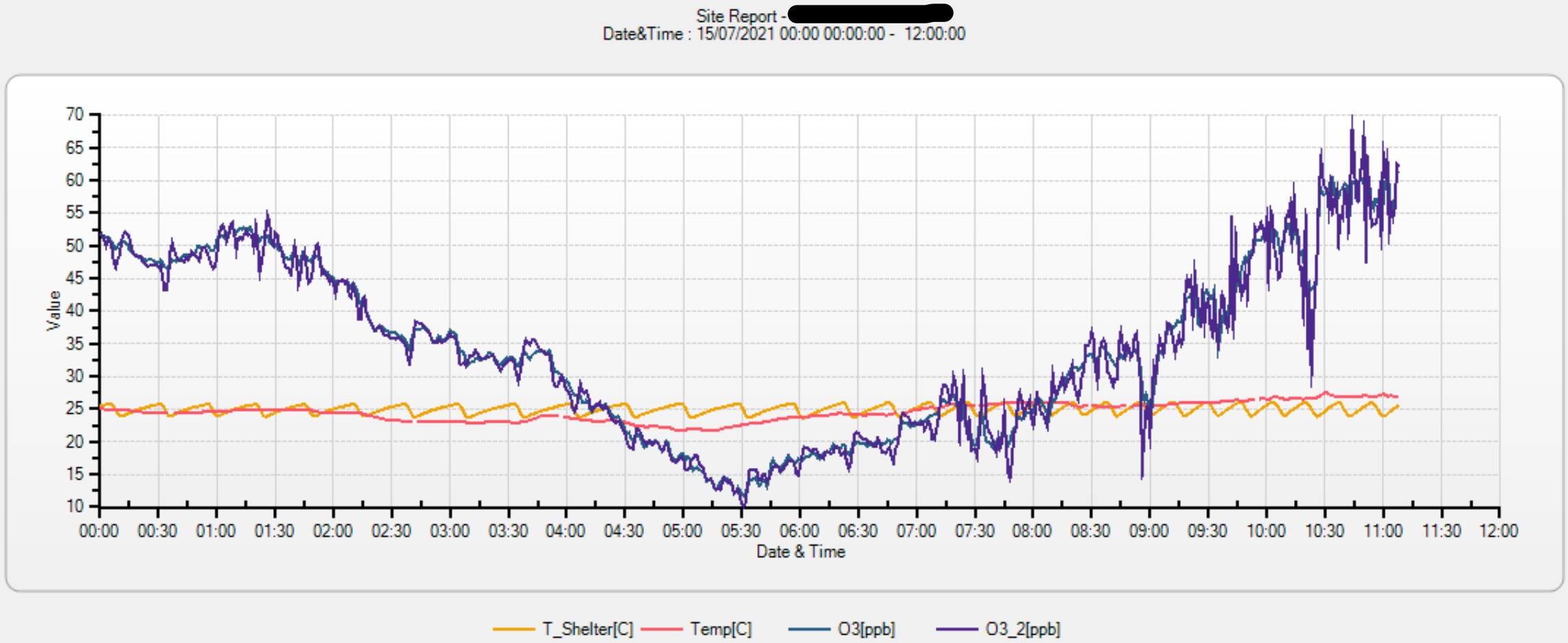
History

- CASTNET implementation approved for addition of external Nafion^{Ż} dryer.
- Requires additional vacuum pump to operate the Nafion^{Ż} dryer.
- Requires additional real estate in the shelter for mounting components.
- No update to FEM designation on analyzer since it's "outside the box"
- Up to end-user to ensure calibration checks are performed through the dryer



EPA CASTNET Photo

Interference from air conditioner Summer in Long Island, NY

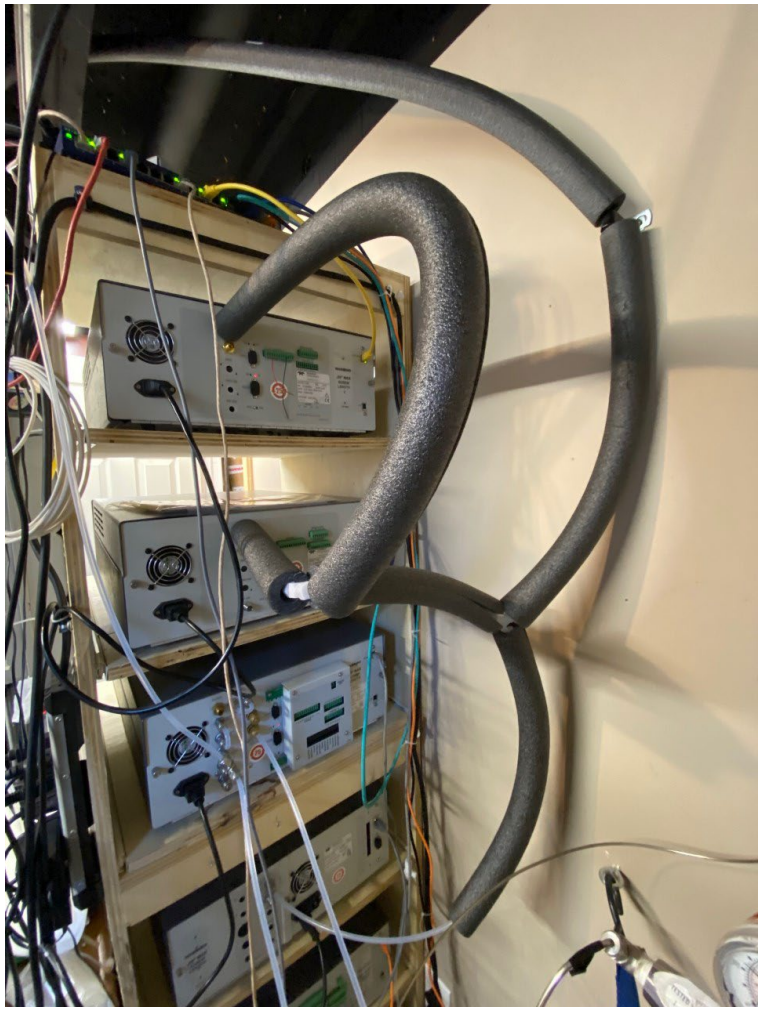


TAPI testing – Winter 21/22 – Fort Collins, CO

- Conduct testing in Fort Collins, CO during Winter of 2021/2022
- Utilize TAPI T400 instruments
- Utilize existing TAPI Nafion^{Ż} dryer product (T265, T200, etc.)
- Follow methodology of CASTNET study

TAPI testing – Winter 21/22 – Fort Collins, CO

- Analyzer in climate-controlled environment
- Insulated 3/8” O.D. Teflon sample line to maintain ambient temp and RH
- Through-the-probe calibrations
- MODBUS TCP/IP data collection and calibrator control at 5-second rate
- Automated ZSP checks, nightly from 02:45 – 03:15, with 10-minute phases at levels 0, 120 and 50 PPB



Configuration

- Dryer purge flow at 800 cc/min for 1:1 ratio sample/purge
- Shares analyzer sample pump and flow control
- Purge air through analyzer filter (long-life 0.01-micron DFU) to extend dryer life
- Utilizes same components as TAPI T265, US EPA approved FRM ozone analyzer
- Follows methodology described in CASTNET study

Configuration

- Control analyzer T400 with no Nafion^{Ż} dryer
- Test analyzer T400 with Nafion^{Ż} dryer
- T703U calibrator for daily checks for both instruments
- Campbell Scientific CR6 DAS for data collection and control
- Vaisala HMP50 for ambient relative humidity and temperature
- Thermocouple for station temperature

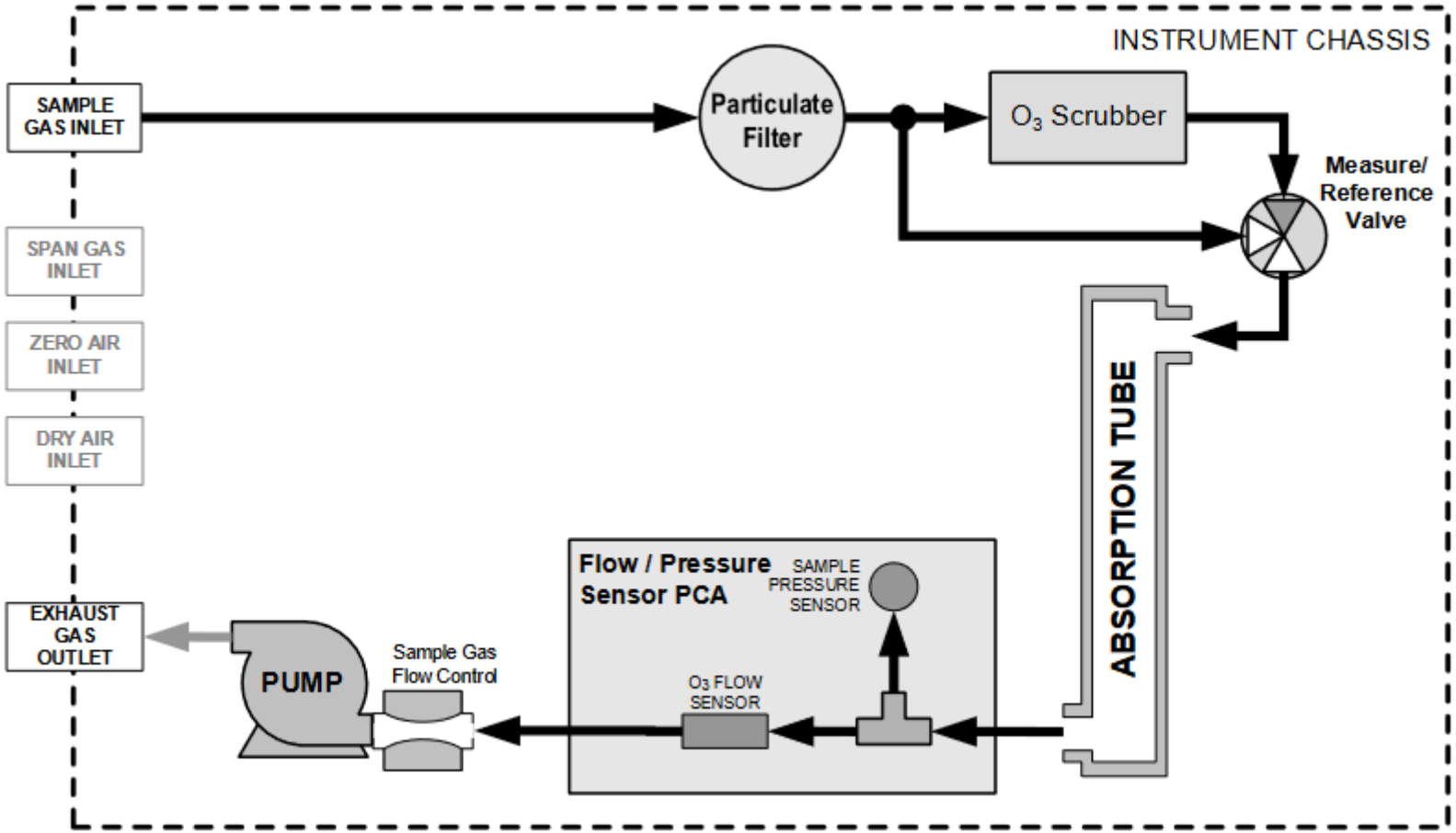
Configuration

- Instruments run in parallel to establish comparison between unmodified instruments.
- Test instrument modified with internal Nafion^{Ż} dryer and run in parallel to the unmodified control instrument.
- Automated daily checks performed at zero, 70 and 120 ppb using T703U reference photometer/generator.
- All instrument data (including T703U) collected via TCP/IP MODBUS and stored at 1-minute and 60-minute resolutions.

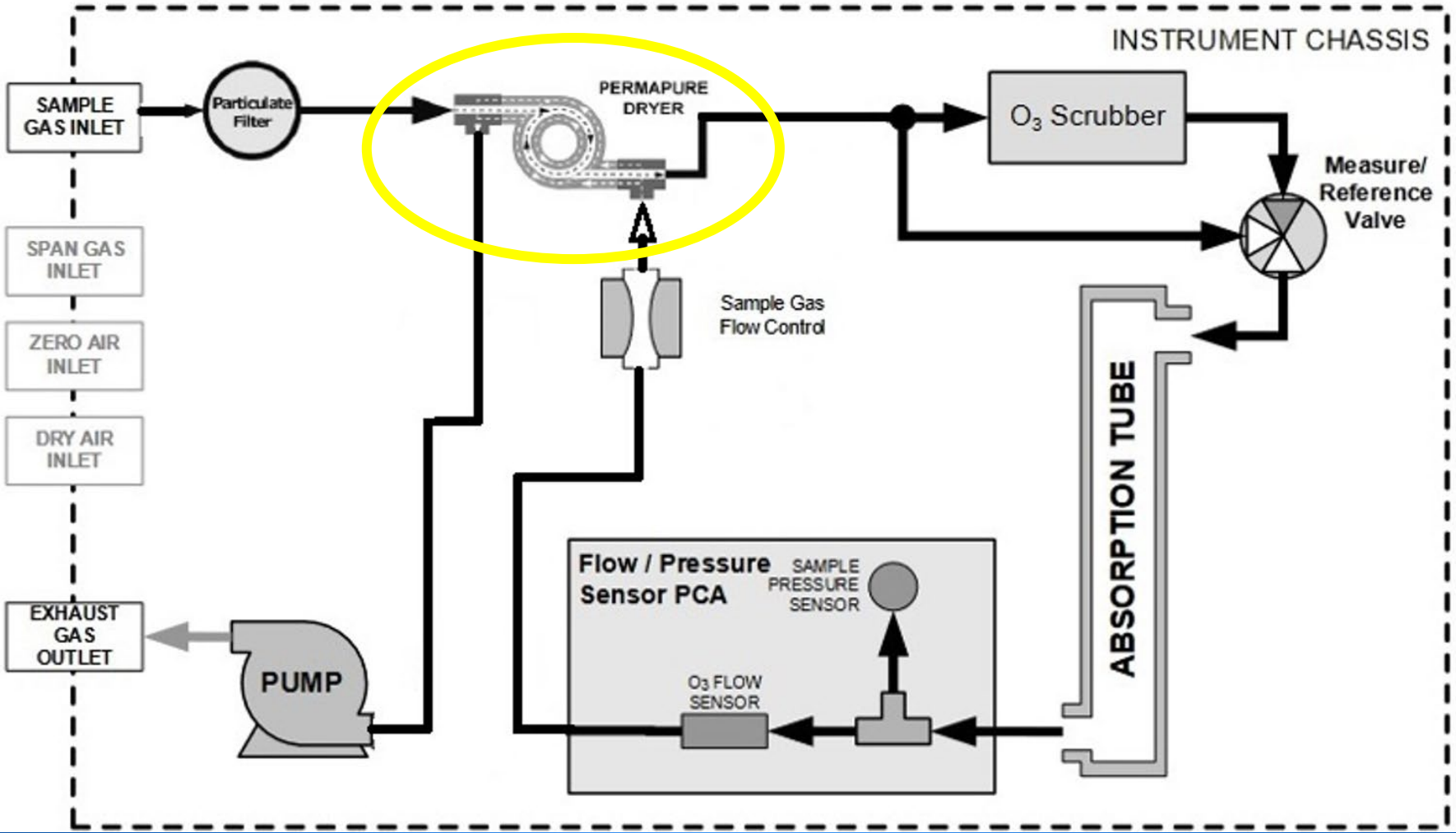
Design and Operating Specifications

Parameter	Specification
Tested UV-based O3 analyzer	TAPI T400 FEM (EPA designation EQOA-0992-087)
Analyzer sample and Dryer purge flow	800 cc/m (use same flow control)
Nafion Dryer Assembly	TAPI 008140000, PermaPure MD-110-03-25
Nafion tube length	~ 6’
Nafion sample air tube ID	1/8”
Nafion sample air residence time	~ 1 second
Purge air to sample air flow ratio	1:1
Purge air inlet filter	Same as sample, FL-50 or 47mm Teflon
Vacuum pump	Uses analyzer vacuum pump

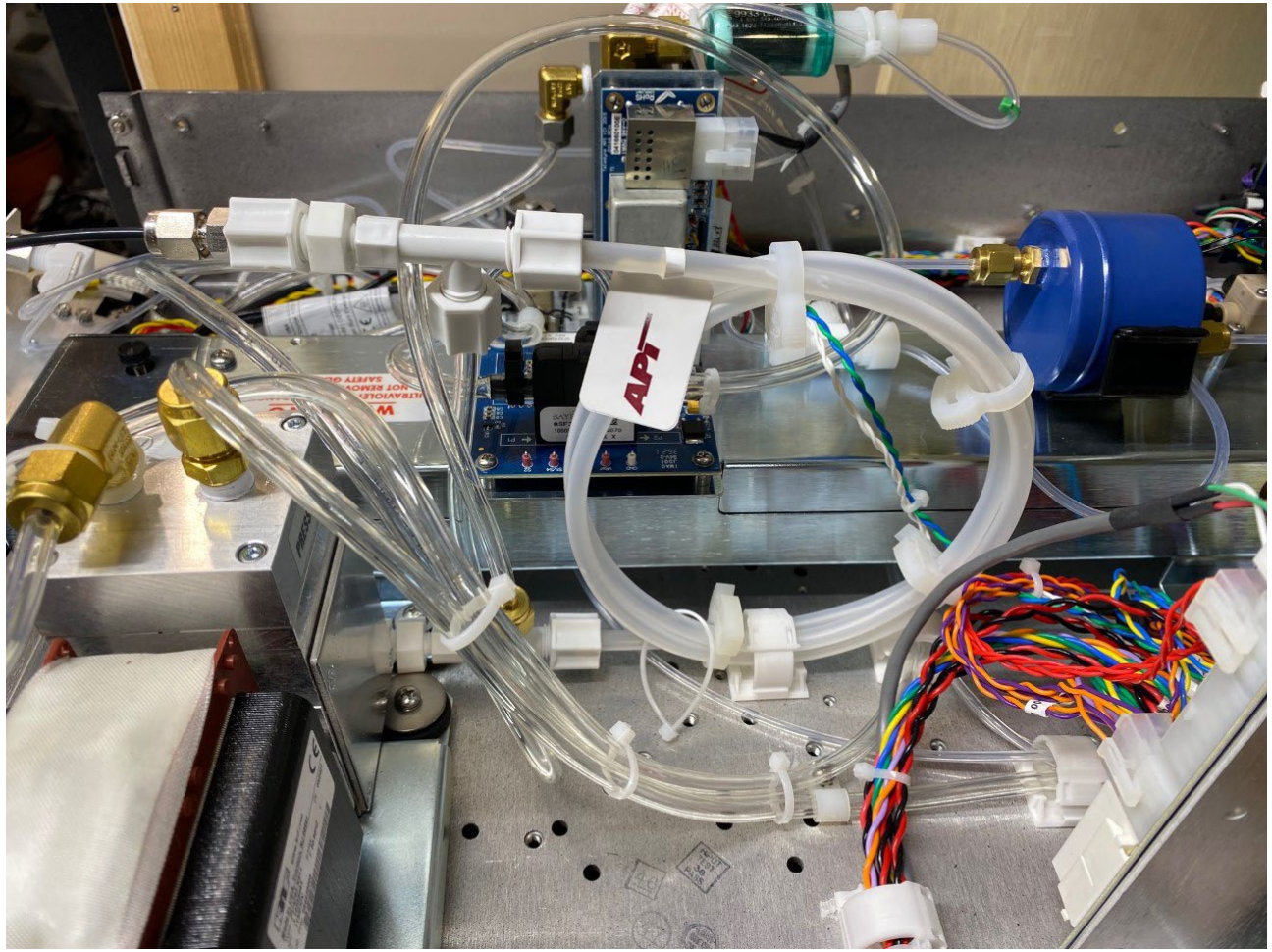
Factory Pneumatics, T400 base

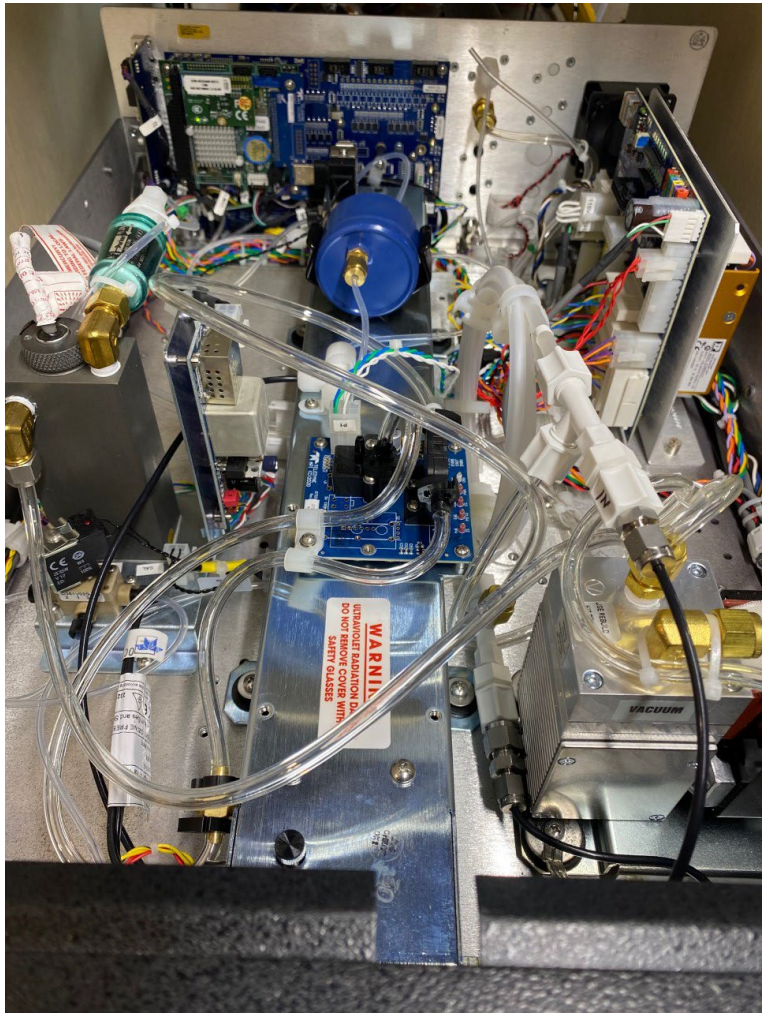


Pneumatics using sample air for dryer

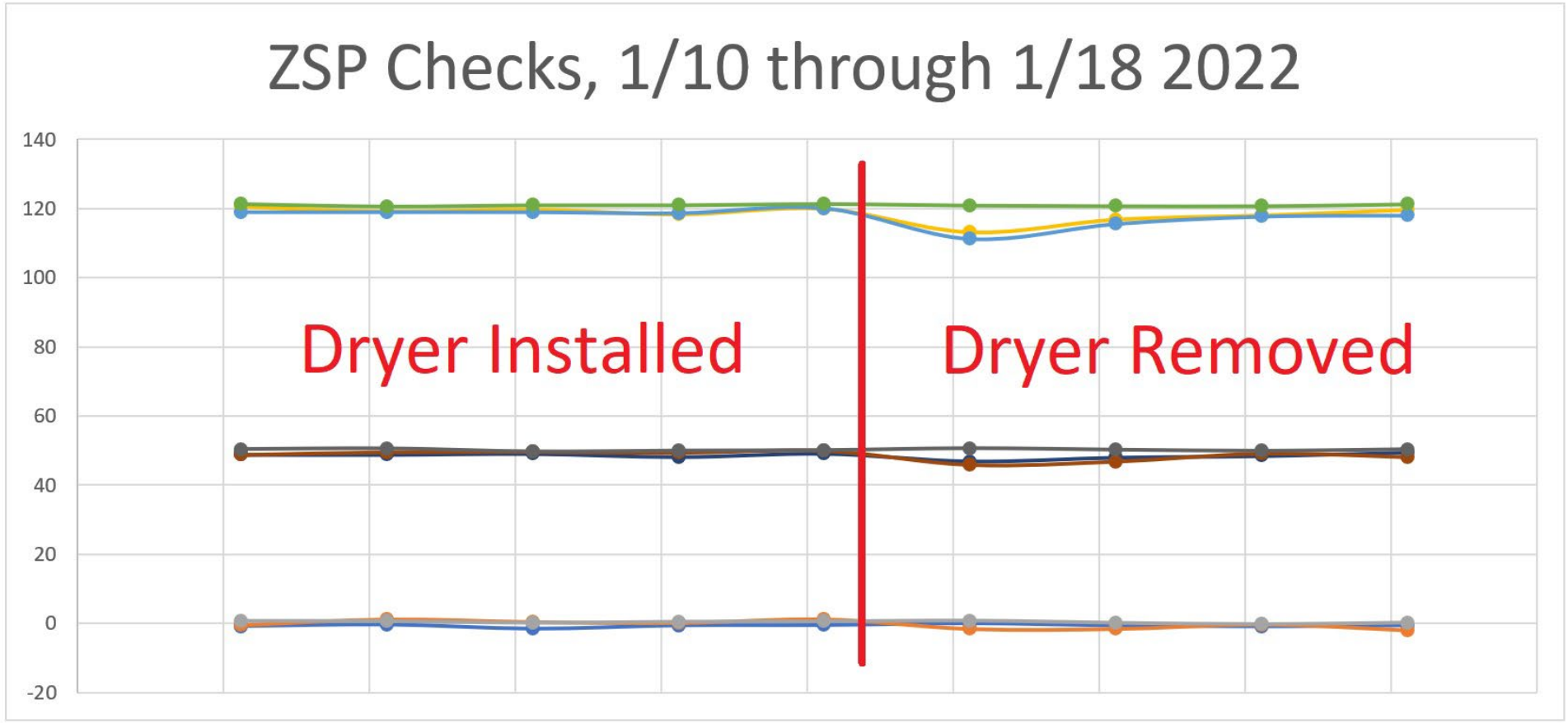


Pneumatics – Nafion™ Dryer





Calibration Checks



- Red bar indicates removal of NafionŻ Dryer from T400_B
- No calibration performed, i.e. same slopes/offsets throughout this period

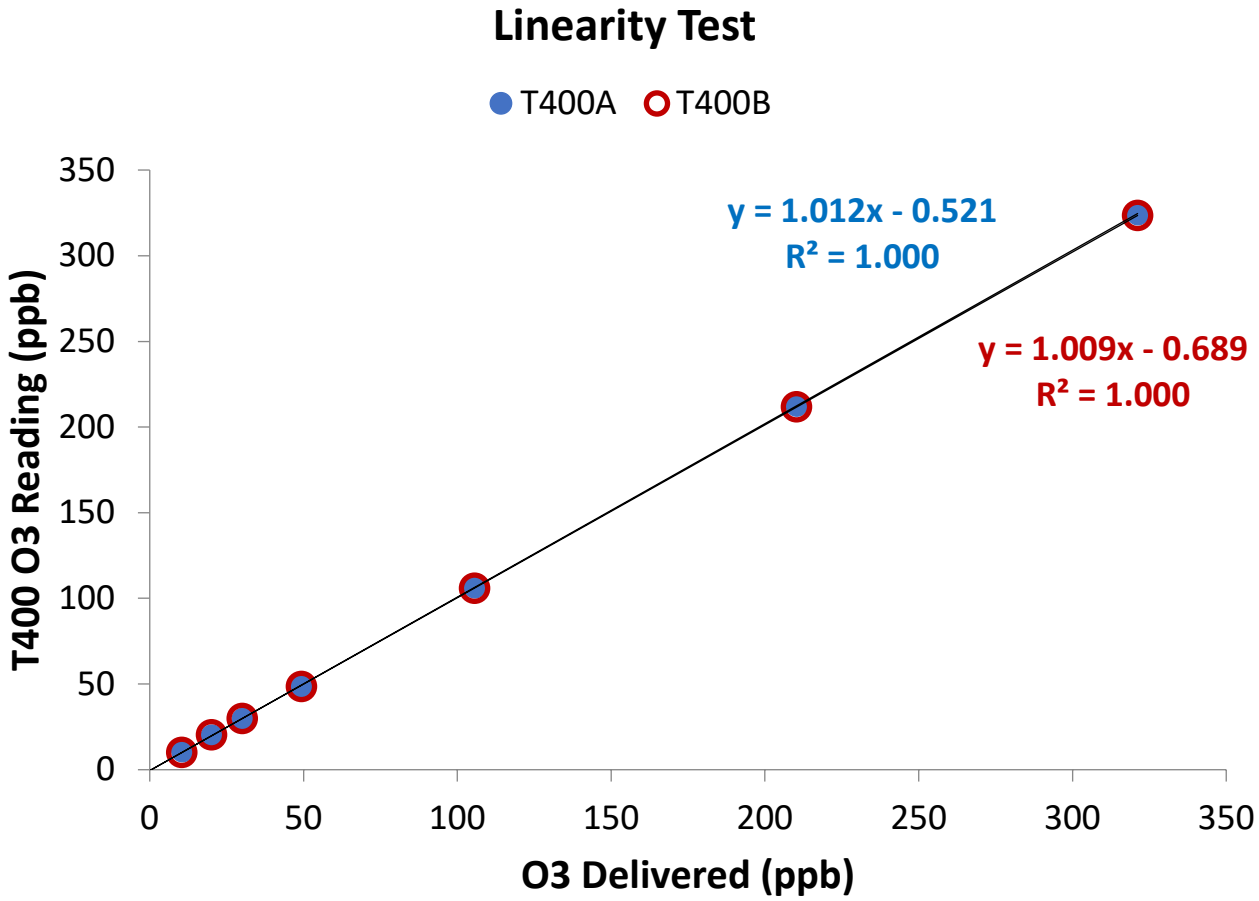
Calibration Checks

T400A_Error			T400B_Error			
ZERO (ppb)	SPAN (%)	PREC (%)	ZERO (ppb)	SPAN (%)	PREC (%)	
-1.5	-0.7	-3.0	-1.2	-2.0	-3.2	Nafion
-1.0	-1.2	-3.4	0.5	-1.3	-2.1	
-1.8	-1.1	-1.2	0.2	-1.7	-0.2	
-1.1	-2.2	-3.6	-0.3	-1.9	-1.2	
-1.1	-1.2	-1.8	0.6	-1.1	-0.3	
-0.8	-6.5	-7.5	-2.3	-7.9	-9.4	Factory
-0.9	-3.2	-4.4	-1.8	-4.2	-6.7	
-0.8	-2.2	-2.8	-0.2	-2.5	-1.5	
-0.9	-1.4	-1.5	-2.2	-2.7	-4.4	

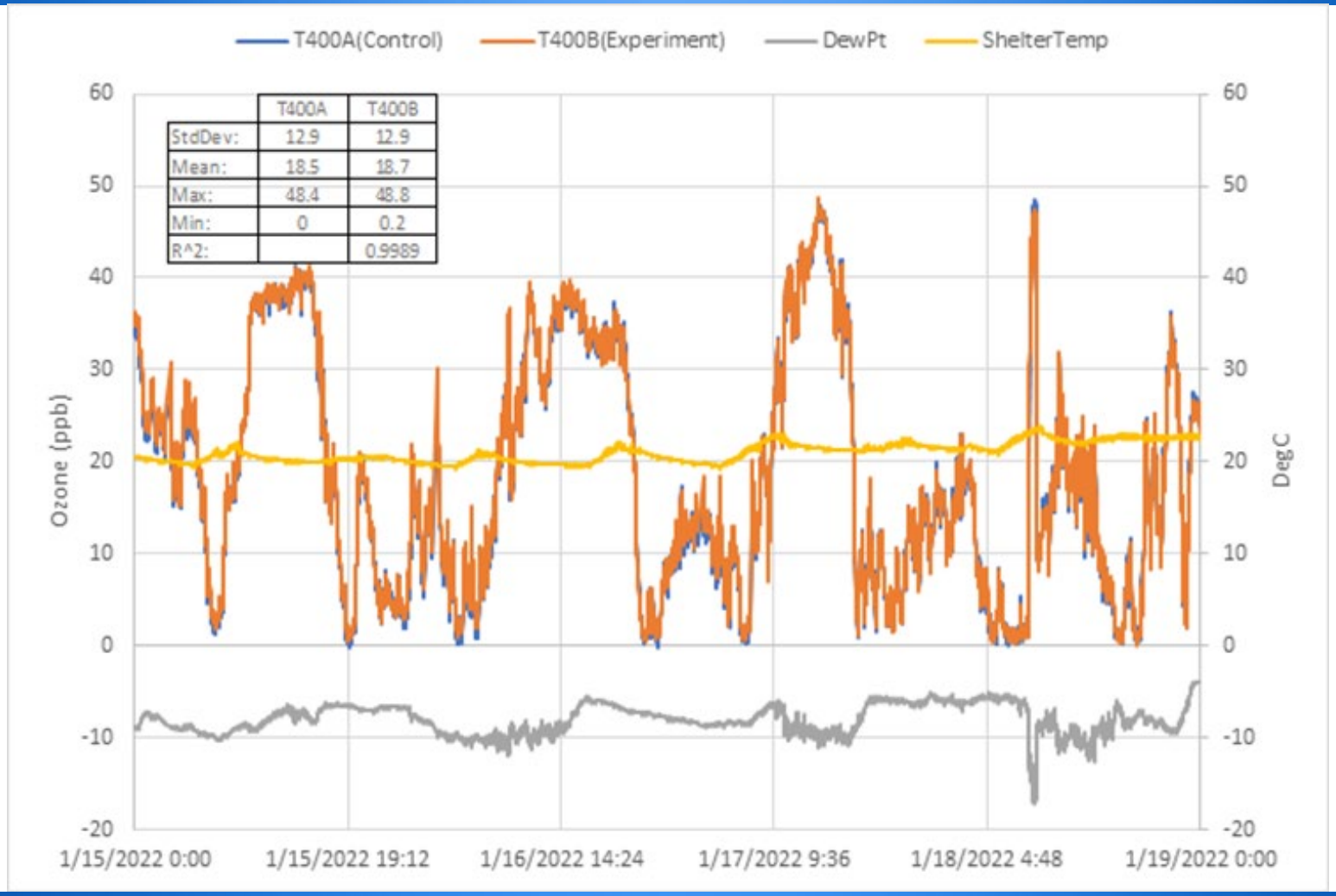
- Checks failed first day after removing Nafion^{Ż} dryer while system equilibrated
- No change in offset/slope before/after

Linearity Testing

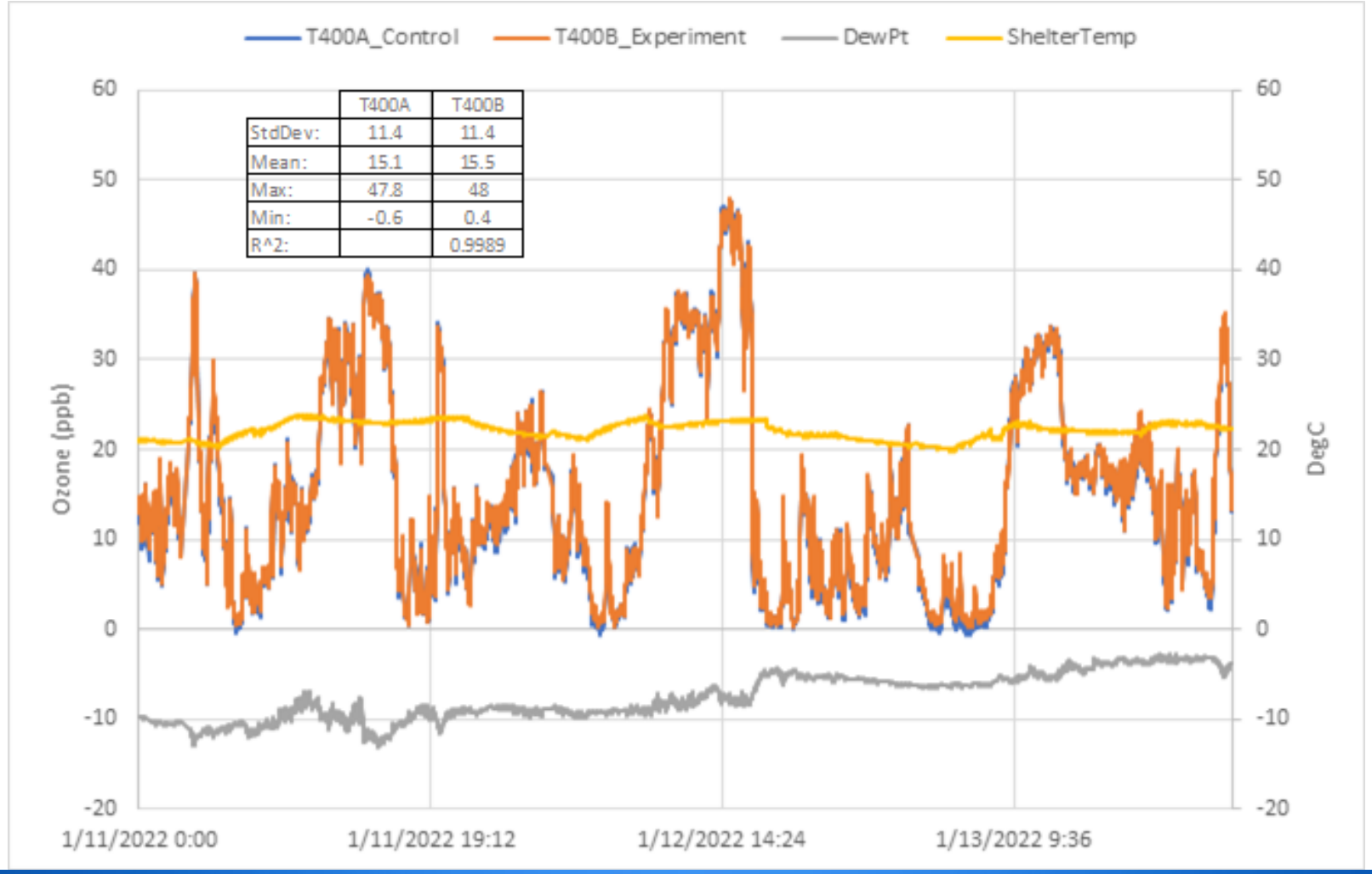
- T400A (Control) vs T400B (with Nafion™)
- Conducted over normal ambient range
- Simultaneous sampling from T703U calibration standard



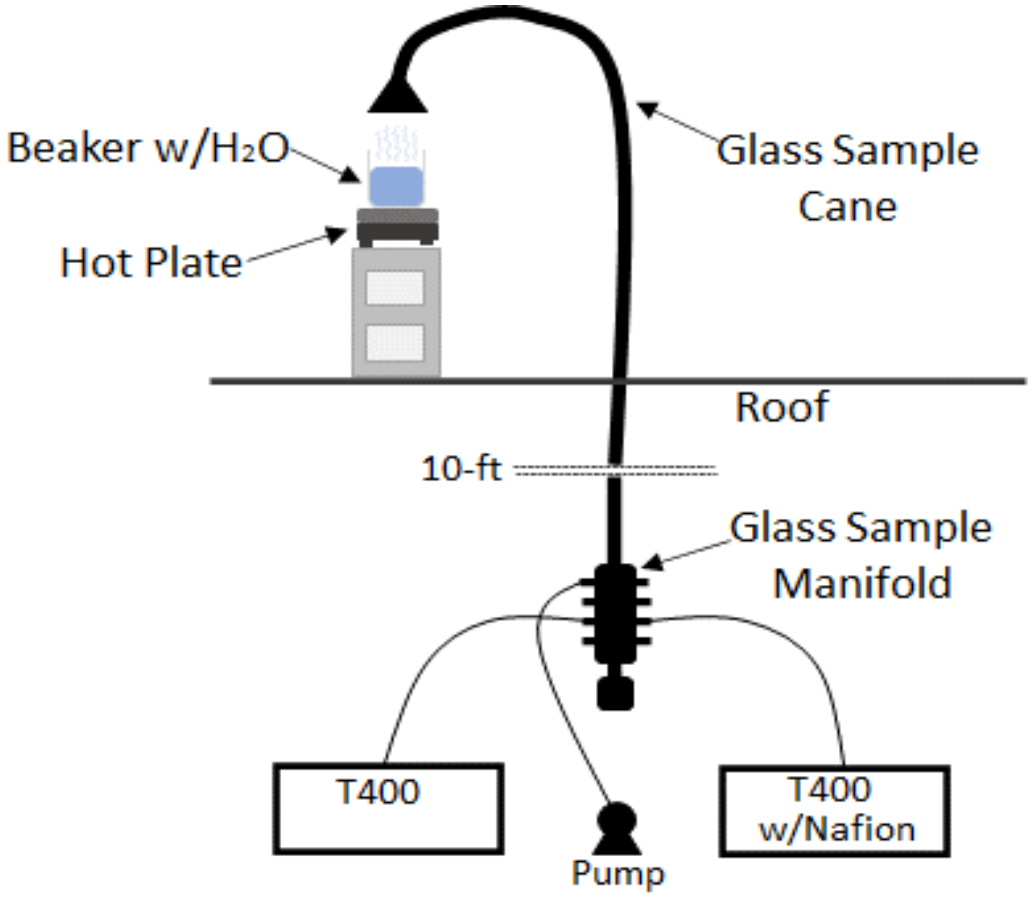
3-day Ambient Comparison, Factory

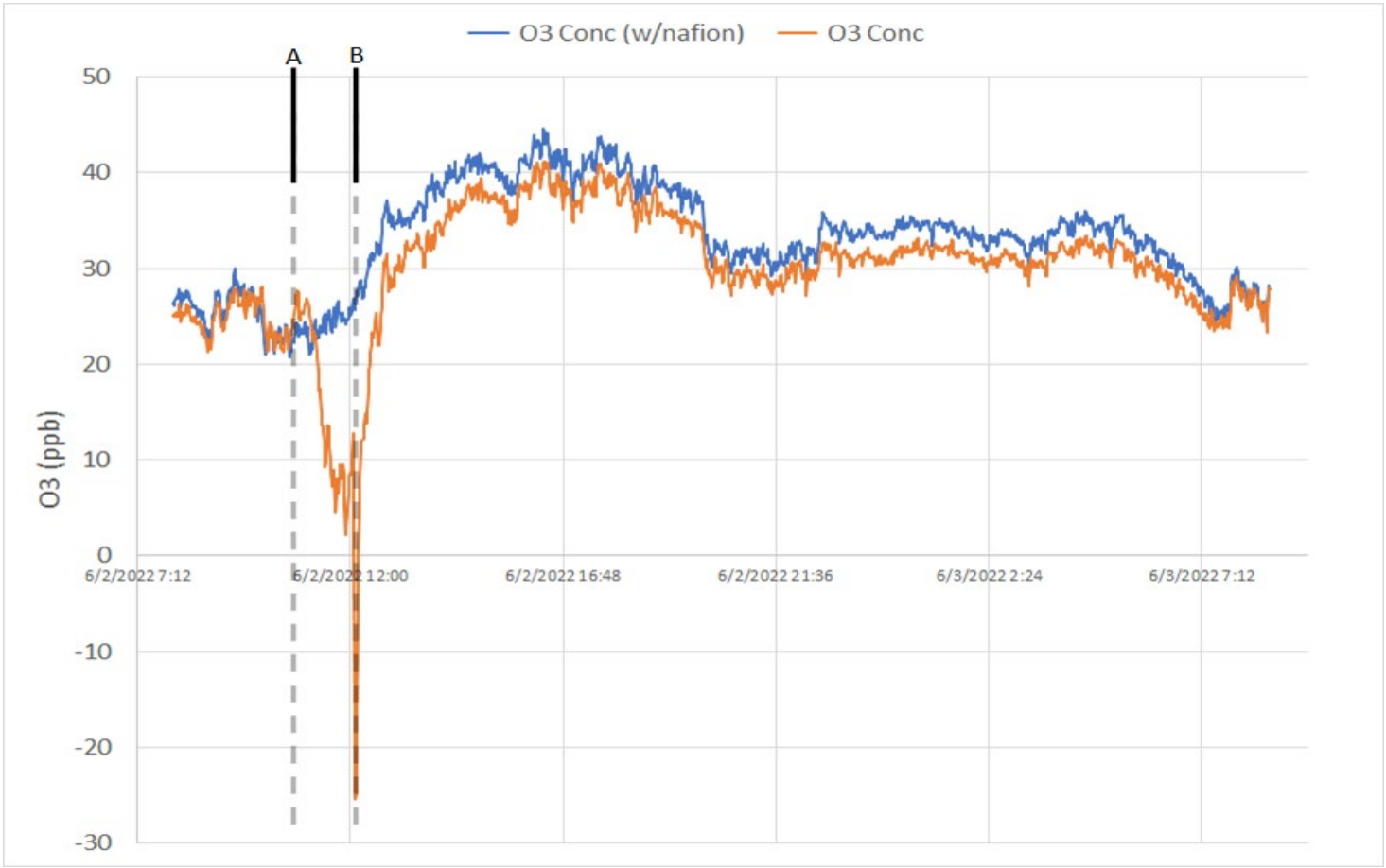


3-day Ambient Comparison, Modified

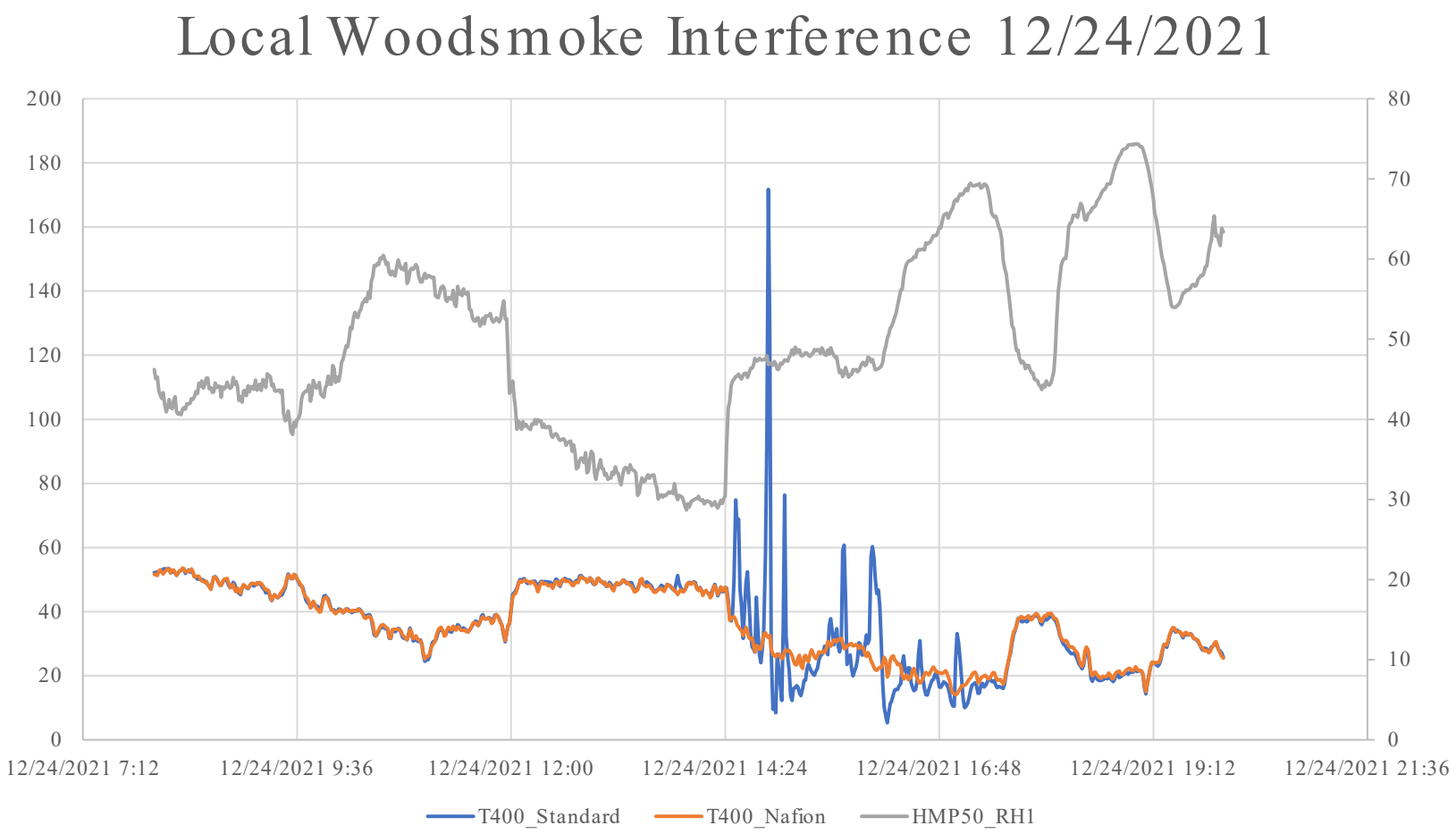


Experimental High Dewpoint Testing





Dec 24, 2021: Woodsmoke Event



	T400A	T400B
StdDev:	14.2	10.9
Mean:	36.4	36.0
Max:	171.8	53.6
Min:	5.3	14.0
R^2:		0.7851

US EPA Compliance Requirements

- Submit modification request to the existing US EPA FEM Method Designation
- Request should include written rationale for modification request
- Include specific details on the intended changes
  - Hardware
  - Location
  - Flow rates
  - Pneumatics
- Submit side-by-side data from an existing T400 FEM designated instrument and proposed Nafion^{Ż} dryer assembly
- Include specific details on expected service life, recommended cleaning, maintenance and/or replacement intervals

Conclusion & Questions

- Placement of Nafion^{Ż} dryer does not significantly affect calibration of instrument as evidenced by automated nightly calibration checks
- Nafion^{Ż} dryer does not scrub ambient ozone
- Placement of Nafion^{Ż} dryer does improve response during periods of rapid RH change and/or localized woodsmoke
- Exact interferences around woodsmoke require further investigation
- Expectation is that Nafion^{Ż} will mitigate H_20 interference based on previous studies by others

Updated Designation EQOA-0992-087

***Teledyne Advanced Pollution Instrumentation, Model 400E or T400 or N400; Advanced Pollution Instrumentation, Model 400/400A; Teledyne Monitor Labs sensor-e™ Model TML-10 Ozone Analyzers; or recordum* airpointer® system module 801-004000;**
Automated Equivalent Method: EQOA-0992-087

"Teledyne Advanced Pollution Instrumentation. Model 400E or T400 or N400; Advanced Pollution Instrumentation, Model 400 or 400A; or Teledyne Monitor Labs sensor-e™ Model TML-10 Ozone Analyzer" operated on any full scale range between 0-100 ppb[1] and 0-1000 ppb, with any range mode (Single, Dual, or AutoRange), at any ambient temperature in the range of 5°C to 40°C (0°C -45°C for the N400), and with a TFE filter or a Kynar® DFU. **Models 400E, T400, N400 and TML-10:** operated with a sample flow rate of 800 ± 80 cm^3/min (measured volumetrically at actual T & P conditions), with the dilution factor set to 1, with Dynamic Zero ON or OFF, with Dynamic Span OFF, with Temp/Press compensation ON, and with or without any of the following options: Internal or external sample pump, Sample/Cal valve option, Internal Zero/Span (IZS), Rack mount with or without slides, analog input option, 4-20 mA isolated current loop output; the NumaView™ software.[2] **Models 400E, T400 and N400**: operated with or without the internal sample dryer assembly (TAPI 008140000).

References

- **Recommendations for Nationwide Approval of Nafion® Dryers Upstream of UV-Absorption Ozone Analyzers, November 16, 2020**: https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=541625&Lab=CEMM
- **Use of Nafion Dryers for Ultraviolet (UV) Ozone Analyzers, February 19, 2021**: https://www.epa.gov/sites/default/files/2021-03/documents/nafion_dryer_memo-_pdf.pdf

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